

# CEE 680: Water Chemistry

Lecture #10

Acids & Bases: Analytical Solutions with  
simplifying assumptions IV  
(Stumm & Morgan, Chapt.3 )

(Benjamin, Chapt. 4)

# Bases: Sodium Acetate Example

$10^{-3}$  M in 1 L

- 1. List all species present



- 2. List all independent equations

- equilibria

- $K_a = [H^+][Ac^-]/[HAc] = 10^{-4.77}$  **1**

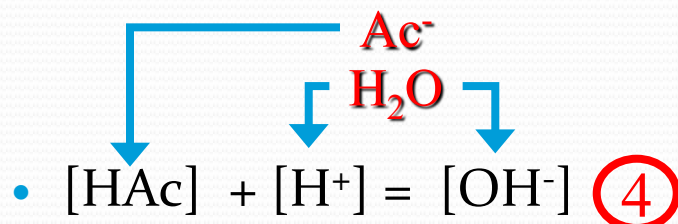
- $K_w = [H^+][OH^-] = 10^{-14}$  **2**

- mass balances

- $C = [HAc] + [Ac^-] = 10^{-3}$  **3**

$$C_{Na} = [Na^+] = 10^{-3} \quad \mathbf{5}$$

- proton balance:  $\Sigma(\text{proton rich species}) = \Sigma(\text{proton poor species})$



$$C_{\text{Na}} = [\text{Na}^+] = 10^{-3} \quad (5)$$

# NaAc Example (cont.)

- 3. Combine equations and solve for  $\text{H}^+$

$$(2) \quad K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{OH}^-] = K_w / [\text{H}^+]$$

$$(4) \quad [\text{H}^+] = [\text{OH}^-] - [\text{HAc}]$$

$$(2+4) \quad [\text{H}^+] = K_w / [\text{H}^+] - [\text{HAc}]$$

$$[\text{H}^+] = K_w / [\text{H}^+] - [\text{H}^+]C / \{K_a + [\text{H}^+]\}$$

$$[\text{H}^+]^2 = K_w - C[\text{H}^+]^2 / \{K_a + [\text{H}^+]\}$$

$$K_a[\text{H}^+]^2 + [\text{H}^+]^3 = K_w K_a + K_w [\text{H}^+] - C[\text{H}^+]^2$$

$$[\text{H}^+]^3 + \{C + K_a\}[\text{H}^+]^2 - K_w[\text{H}^+] - K_w K_a = 0$$

$$(3) \quad C = [\text{HAc}] + [\text{Ac}^-]$$

$$[\text{Ac}^-] = C - [\text{HAc}]$$

$$(1) \quad K_a = [\text{H}^+][\text{Ac}^-] / [\text{HAc}]$$

$$(1+3) \quad K_a = [\text{H}^+]\{C - [\text{HAc}]\} / [\text{HAc}]$$

$$K_a[\text{HAc}] = [\text{H}^+]C - [\text{H}^+][\text{HAc}]$$

$$[\text{HAc}] = C[\text{H}^+] / \{K_a + [\text{H}^+]\}$$

- 4. Solve for other species

# Answer

- $[\text{OH}^-] = 7.67 \cdot 10^{-7}$
- $\text{pOH} = 6.115$
- $\text{pH} = 7.885$

# In-class Practice

- $10^{-4}\text{M}$  Sodium Acetate

- UMass: Alvin & Cielo, Chris
- UNISA: Sikelelwa

- $10^{-3}\text{M}$  Sodium Cyanide

- UMass: Ian & JQ
- UNISA:

- $10^{-3}\text{M}$  Calcium Oxalate

- UMass:
- UNISA: Alfred

- $10^{-4}\text{M}$  Sodium Bicarbonate

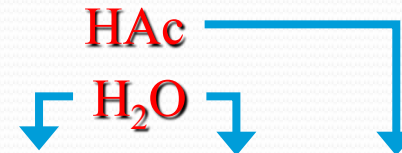
- UMass: Laura, Bridgette, Isaac
- UNISA:

**For Oxalic acid,**  
 $\text{H}_2\text{Ox} \leftrightarrow \text{HOx}^- \leftrightarrow \text{Ox}^{2-}$   
**pKa1=1.25**  
**pKa2=4.27**

*Note: Alkali metals such as Na and K do not act as acids, so they are ignored here*

# Writing PBE's

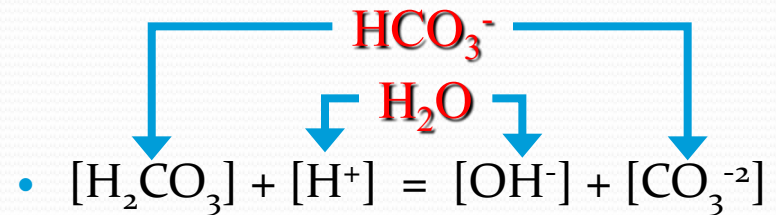
- Monoprotic Acid
  - same as ENE
- Diprotic Acid
  - same as ENE
- Diprotic: Ampholyte
  - Not ENE
    - e.g.,  $\text{NaHCO}_3$
- Diprotic Base
  - Not ENE



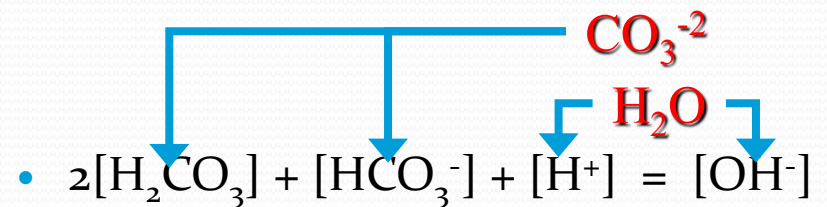
- $[\text{H}^+] = [\text{OH}^-] + [\text{Ac}^-]$



- $[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{-2}]$



- $[\text{H}_2\text{CO}_3] + [\text{H}^+] = [\text{OH}^-] + [\text{CO}_3^{-2}]$



- $2[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{H}^+] = [\text{OH}^-]$

# Guide to Simplified Acid/Base Solutions #1

- Neutral

$$[H^+] \approx \sqrt{K_w}$$

- if  $C < 10^{-8}$

- Acid Addition,  $C > 10^{-6.5}$

- Acidic

- if  $K_a C > 10^{-13}$

$$[H^+] \approx \frac{-K_a + \sqrt{K_a^2 + 4K_a C}}{2}$$

- Strong Acid

- if  $K_a > 10C$

$$[H^+] \approx \frac{C + \sqrt{C^2 + 4K_w}}{2}$$

- Weak Acid

- if  $C > 100K_a$

$$[H^+] \approx \sqrt{K_a C + K_w}$$

$$[H^+] \approx C$$

$$[H^+] \approx \sqrt{K_a C}$$

# Guide to Simplified Acid/Base Solutions #2

- Base Addition,  $C > 10^{-6.5}$

- Basic

- if  $K_b C > 10^{-13}$

$$[OH^-] \approx \frac{-K_b + \sqrt{K_b^2 + 4K_b C}}{2}$$

- Strong Base

- if  $K_b > 10C$

$$[OH^-] \approx \frac{C + \sqrt{C^2 + 4K_w}}{2}$$

- Weak Base

- if  $C > 100K_b$

$$[OH^-] \approx \sqrt{K_b C + K_w}$$

$$[OH^-] \approx C$$

$$[OH^-] \approx \sqrt{K_b C}$$

- Very Dilute Systems

- if  $10^{-8} < C < 10^{-6.5}$

- try strong acid/base or weak acid/base assumption
- otherwise may need to use general solution



# Exact Solutions: Summary

- Monoprotic

- Acids:  $[H^+]^3 + K_a[H^+]^2 - \{K_w + K_a C\}[H^+] - K_w K_a = 0$

- Bases:  $[H^+]^3 + \{C + K_a\}[H^+]^2 - K_w[H^+] - K_w K_a = 0$

- Diprotic

- Acids:

- $[H^+]^4 + K_1[H^+]^3 + \{K_1 K_2 - K_w - K_1 C\}[H^+]^2 - K_1 \{2CK_2 + K_w\}[H^+] - K_w K_1 K_2 = 0$

- Ampholytes:

- $[H^+]^4 + \{C + K_1\}[H^+]^3 + \{K_1 K_2 - K_w\}[H^+]^2 - K_1 \{CK_2 + K_w\}[H^+] - K_w K_1 K_2 = 0$

- Bases:

- $[H^+]^4 + \{2C + K_1\}[H^+]^3 + \{CK_1 + K_1 K_2 - K_w\}[H^+]^2 - K_1 K_w [H^+] - K_w K_1 K_2 = 0$



- To next lecture